

MODELING AND CONTROL OF QUARTZ CRYSTAL OPERATED IN LIQUID
FOR BIO-SENSING APPLICATION

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DEDICATION

*To my uncle Khudhair Abbas Dawood: Thank you for your
unconditional support with my studies.*

*I am honored to have you as my uncle. Thank you for giving me a
chance to prove and improve myself.*

To my beloved family



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PERPUSTAKAAN TUNKU TUN AMINAH

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All praise for Allah, blessing to Prophet Muhammad S.A.W along with his family and friends.

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ABSTRACT

Nowadays the applications of sensors are a very promising research field since they find application in many different areas. Biosensors are an increasingly important technology in the detection of compounds ranging from pesticides to biological weapons. Typically, biosensors consist of a biological macromolecule that is immobilized on the surface of a signal transducer. As the macromolecule binds specifically to the ligand being detected, the signal transducer can measure a physical change due to the binding event. One promising type of detector is the Quartz Crystal Microbalance (QCM). The QCM is a piezoelectric mass-sensing device. A QCM device works by sending an electrical signal through a gold-plated quartz crystal, which causes a vibration at some resonant frequency. The QCM then measures the frequency of oscillation in the crystal. When used as a biosensor, the QCM can detect changes in frequency of the crystal due to changes in mass on the surface of the crystal. In the present work, all related equations and data base related to biosensors piezoelectric devices will be considered in the developed model. The model will describe biosensors limitations and capacities together with measurement resolutions and errors. The work will includes build of software program using Microsoft visual studio C# 2010.net frame work 4.0 and all available theoretical and empirical formulas and program data base will include the data for QCM sensors and resonance frequencies, this program will include all cases needed to be studied for the present work (bio sensing). Many sensors can be used for QCM, the present work will be limited to TSM sensors, and the proposed software for Bio-sensing. The frequency signal is detected by a frequency counter and processed electronically in a separate computer. The QCM sensor used is 19.5 MHZ using buffer media in the testing procedure. The result according to z-methods indicates that while the resonance frequencies increase the small amount of despite material can be easily detected. With the data extracted for (5 MHZ) sensors with effective area of 14 mm^2 , the results show that as the change in resonance frequency increase as the despite material increase. The film thickness of deposit material increase as the natural frequencies of sensors decreased.

ABSTRAK

Aplikasi sensor pada masa kini merupakan salah satu cabang penyelidikan yang boleh diaplikasikan dalam pelbagai bidang. Bio-sensor merupakan teknologi penting dalam mengesan campuran samada terdiri daripada racun perosak mahupun senjata biologi. Kebiasaannya, biosensor ini terdiri daripada makromolekul biologi yang mampu bergerak di permukaan transduser isyarat. Apabila makromolekul yang mengikat ligan dikesan, transduser isyarat akan mengesan perubahan dan mengukur perubahan fizikal yang disebabkan proses peyatan tersebut. Transduser biasanya mengesan perubahan dalam rintangan, pH, haba, cahaya, atau jisim dan kemudiannya menukar data tersebut kepada isyarat elektrik untuk dikumpul dan diproses. Salah satu jenis pengesan adalah “Quartz Crystal Microbalance” (QCM). QCM ini ialah sejenis peranti pengesan piezoelektrik yang berfungsi menghantar isyarat elektrik melalui kristal kuarza yang disaluti emas dan kemudian menyebabkan getaran pada frekuensi salunan. Kemudian QCM akan mengukur kekerapan ayunan dalam kristal. QCM juga boleh berfungsi sebagai biosensor bagi mengesan perubahan frekuensi kristal yang disebabkan oleh perubahan jisim di permukaan kristal tersebut. Kajian ini juga merangkumi pembinaan perisian dengan menggunakan Microsoft visual studio C# 2010.net frame work 4.0 serta kesemua teori dan formula-formula empirikal serta program pangkalan data termasuk data-data untuk pengesan QCM dan salunan frekuensi. Program ini juga akan mengambil kira semua kajian berkenaan dengan bio-sensing. Walaupun terdapat banyak jenis pengesan yang boleh digunakan untuk QCM, namun kajian ini akan menghadkan focus terhadap pengesan jenis TSM dan perisian yang dicadangkan untuk bio-sensing. Isyarat frekuensi yang dikesan pengira kekerapan akan diproses secara elektronik di computer yang berbeza. Pengesan QCM yang digunakan ialah 19.5 MHZ dan menggunakan media disambiguasi pada prosedur pengujian. Hasil kajian menurut kaedah-z menunjukkan peningkatan salunan frekuensi dalam jumpah yang kecil boleh dikesan dengan mudah. Data-data yang diekstrak (5MHZ) untuk pengesan pada luas efektif sebanyak 14 mm² menunjukkan perubahan salunan frekuensi meningkat ketika bahan deposit meningkat. Ketebalan filem bahan deposit juga meningkat apabila frekuensi asli pengesan berkurangan.

CONTENTS

TITLE	PAGE
DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
ABSTRAK	vi
CONTENTS	vii
LIST OF FIGURES	x
LIST OF TABLES	xii
LIST OF ABBREVIATION AND SYMBOLS	xiii
LIST OF APPENDIXS	xv
CHAPTER 1 INTRODUCTION	1
1.1 Project Background	1
1.2 Problem Statements	2
1.3 Project Objectives	3
1.4 Project Scopes	3
1.5 Expected Results	4

1.6	Research Significance	4
1.7	Summary	7

CHAPTER 2 LITERATURE REVIEW 8

2.1	Introduction	8
2.2	QCM Systems	11
2.3	Quartz Characteristics	13
2.4	Previous Studies	13
2.5	Summary	15

CHAPTER 3 METHODOLOGY 17

3.1	Introduction	17
3.2	Dissipation factor (D)	22
3.3	Resistance Measurement	22
3.4	Errors in the measurement of R_m	23
3.5	Noise in the measurement of R_m	23
3.6	Calibration of R_m	24
3.7	Z-match Method	25
3.8	Z-Factor of film material	26
3.9	Software Calculations	27

3.10 Summary

CHAPTER 4 RESULTS AND DISCUSSIONS 32

4.1	Calculations software	32
4.2	Theoretical analyses of many biological substances depending upon experimental results	33
4.3	Theoretical approach to measure Beta Amyloid 1-42 peptide using QCM Sensors software program	38
4.4	Sensitivity of QCM sensors	42
4.5	Mass per unit area of Bio material in liquid	44
4.6	Resistance Measurement	46

CHAPTER 5 CONTROL THE PHYSICAL PROPERTIES 48

5.1	Introduction	48
5.2	Transfer Function and Block Diagram	49
5.3	Equivalent circuit model of QCM near resonance with additional impedance representing viscoelastic loading	56

CHAPTER 6 CONCLUSSTIONS AND RECOMMENDATIONS 61

6.1	Conclusions	61
6.2	Recommendations	62

REFERENCES 63

APPENDIX

LIST OF FIGURE

NO.	FIGURES	PAGES
2.1	Schematic of QCM sensor array	11
2.2	Biological sensing method	12
3.1	Flow chart of the project	18
3.2	Sensors can be used for QCM	27
3.3	The proposed software for Bio-sensing	28
3.4	Typical testing measurements	30
4.1	QCM Sensor software program main screen	32
4.2	QCM Sensor software program flow chart	33
4.3	Output experimental results (ohms verses frequency of PAH bio substance), resonance frequency 19.5MHz	34
4.4	Output experimental results (ohms verses frequency of Protein G substance), resonance frequency 19.5MHz	35
4.5	Output experimental results (ohms verses frequency of Antibody), resonance frequency 19.5MHz	35
4.6	Output experimental results ((ohms verses frequency of AD Biomarker)), resonance frequency 19.5MHz	36
4.7	Z method results to calculate elastic film mass with different natural frequencies	39
4.8	Change in elastic film mass with change in frequencies	40
4.9	Deposit film thickness variations with different sensors frequencies	41
4.10	Variations of changes in mass of deposit material with change in natural frequencies	42
4.11	QCM sensors sensitivity with change in natural frequencies	43
4.12	QCM sensors sensitivity of deposited material with natural frequencies	44

4.13	Changes in many natural frequencies due to depositing the same bio material	45
4.14	Change in loaded mass variations for different natural frequencies	46
4.15	Change of resistance with voltage in system of QCM	47
4.16	Variation of dR_m/V_c in system of QCM	47
5.1	BVD equivalent circuit displaying both the parameters and impedance of the circuit elements	49
5.2	Block diagram of QCM system	52
5.3	Bio-material depositing block diagram	52
5.4	Resonance circuit	53
5.5	MultiSIM software Circuit output in frequency domain	54
5.6	Output response to resonance circuit	55
5.7	Resonance circuit with 18.333 MHz	56
5.8	MultiSIM software Circuit output in frequency domain	58
5.9	Output response to resonance circuit	59
5.10	Output response to resonance circuit (difference between load free and loaded sensor frequency)	60



LIST OF TABLES

NO.	TABLE	PAGES
1.1	QCM Applications	6
3.1	The theoretical sensitivity coefficient calculations	29
4.1	Change in oscillation frequencies due to viscoelastic behavior of Biomaterial	37
4.2	Change in mass Δm (ng/cm^2) of different Bio material	37
4.3	Z method results to calculate elastic film mass with different natural frequencies	39
4.4	Change in elastic film mass with change in frequencies	40
4.5	Deposit film thickness variations with different sensors frequencies	41
4.6	Variations of changes in mass of deposit material with change in natural frequencies	42
4.7	QCM sensors sensitivity and change in deposited material with natural frequencies	43
4.8	changes in many natural frequencies due to depositing the same bio material	44
4.9	Change in loaded mass variations for different natural frequencies	45
4.10	Change of resistance with voltage and variation of dR_m/V_c in system of QCM	46
5.1	Typical equivalents circuit values of four uncoated crystals	52

LIST OF ABBREVIATION AND SYMBOLS

Δf	the observed frequency change, in Hz
Δm	the change in mass per unit area, in g/cm^2
C_f	the sensitivity factor for the crystal
n	number of the harmonic at which the crystal is driven
f_o	the resonant frequency of the fundamental mode of the crystal, in Hz
ρ_q	density of quartz – 2.648 g cm^{-3}
μ_q	shear modulus of quartz - $2.947.1011 \text{ g.cm}^{-1}.\text{s}^{-2}$
ρ_f	density of film material, in g/cm^3
T_f	thickness of the film, in cm
f_u	frequency of oscillation of unloaded crystal
ρ_q	density of quartz – $2.648 \text{ g . cm}^{-3}$
μ_q	shear modulus of quartz- $2.947.1011 \text{ g.cm}^{-1}.\text{s}^{-2}$
ρ_L	density of the liquid in contact with the electrode
η_L	viscosity of the liquid in contact with the electrode
D	Dissipation factor
R_m	motional series resonance resistance, in Ω
V_c	conductance voltage output, in V
N_q	Frequency Constant for AT-cut quartz crystal: $1.668 \times 10^{13} \text{ Hz. Å}$
ρ_q	density of quartz: $2.648 \text{ g . cm}^{-3}$
ρ_f	density of film material, in g . cm^{-3}
f_U	Frequency of unloaded crystal (prior to deposition), in Hz
f_L	Frequency of loaded crystal, in Hz
μ_q	shear modulus of quartz: $2.947.1011 \text{ g . cm}^{-1} . \text{s}^{-2}$

μ_f	shear modulus of film material
E_{lost}	the energy lost (dissipated) during one oscillation cycle
E_{stored}	the total energy stored in the oscillator.
f_k	the series resonance frequency
f_λ	the parallel resonance frequency
$Y(\omega)$	the total impedance in frequency domain
G	real part of admittance
B	imaginary part of admittance
Z_m	Uncoated admittance (R_m , C_m , L_m , C_p)
Z_v	Coated admittance (R_1 , L_1)



LIST OF APPENDIXS

NO.	TITLE	PAGES
1	Calculations Software Input and output Sheets	68
2	QCM Biosensors Equipment	78
3	QCM sensor software code	84



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CHAPTER 1

INTRODUCTION

1.1 Project Background

The technical formula of Quartz-crystal is SiO_2 and it is composed of two elements, silicon and oxygen. In its amorphous form SiO_2 is the major constituent in many rocks and sand. The crystalline form of SiO_2 or quartz is relatively abundant in nature, but in the highly pure form required for the manufacture of quartz crystal units, the supply tends to be small.

The limited supply and the high cost of natural quartz have resulted in the development of a synthetic quartz manufacturing industry. Synthetic quartz crystals are produced in vertical autoclaves. The autoclave works on the principle of hydrothermal gradients with temperatures in excess of $400\text{ }^{\circ}\text{C}$ and pressures exceeding 1,000 atmospheres [1]. Seed quartz crystals are placed in the upper chamber of the autoclave with natural quartz being placed in the lower chamber. An alkaline solution is then introduced which when heated increases the pressure within the chamber. The autoclave heaters produce a lower temperature at the top chamber in comparison to the bottom. This temperature gradient produces convection of the alkaline solution which dissolves the natural quartz at the bottom of the chamber and deposits it on the seed crystals at the top. Alpha crystals produced by this method can have masses of several hundred grams and can be grown in a few weeks. If the temperature reaches $573\text{ }^{\circ}\text{C}$ a phase transition takes place which changes the quartz from an alpha to a beta (loss of piezoelectric property).

Quartz crystals are an indispensable component of modern electronic technology. They are used to generate frequencies to control and manage virtually all communication systems. They provide the isochronous element in most clocks, watches, computers and microprocessors. The quartz crystal is the product of the phenomenon of piezo-electricity discovered by the Curie brothers in France in 1880 [1].

1.2 Problem Statements

One of very promising applications of acoustic wave sensors is the measurement of small amounts of chemical and biological substances in liquids. A high sensitivity regarding mass loading is expected to be achieved due to the usage of shear waves because of their low interaction with the contacting fluid. As a consequence of their extraordinary properties quartz resonators can be found in all kinds of electronic devices, such as watches and computers to give an accurate time base, and as signal generators of reference systems in electronic devices.

Quartz resonators did not become of interest commercially until immediately prior to the world war. The development of new measurement technique represents one of the major driving forces in biotechnology that positively impact related research areas such as polymer characterization and biochemistry and is critical to the evolution of the pharmaceutical, biotechnology and biomaterial industries. Piezoelectric effect is a reversible of generation of internal electrical charges (or electrical field) in response to mechanical deformation of the material, or vice versa. Typically piezo sensors operate in dry conditions either in gases or a vacuum and are based on direct relationship of added mass and oscillation frequency given Sauerbrey equation.

Quartz crystal microbalance (QCM) sensors have become a valuable tool for the study of material properties with respect to fluids or solid films. The spectrum of applications related to the use of QCM sensors is continuously broadening, as it is evident from the ever increasing body of published articles in interdisciplinary scientific areas such as thin film materials, electrochemistry, and biosensors [2].

1.3 Project Objectives

This study embarks on the following objectives:

1. To study quartz crystal microbalance system, characteristics and properties.
2. To investigate the impedance spectra for AD Biomarker and Beta Amyloid 1-42 peptide antibodies using a developed modeling software.
3. To control the physical properties of the crystal based on the impedance characteristics by using Butterworth Van dyke (BVD) modeling software.

1.4 Project Scopes

The scopes of this project are comprise the boundaries of project study. Many scopes should be bound in order to make this project achieve the objectives.

1. Develop a mathematical model for quartz crystal system, Crystal oscillation ranged between 5 to 30 MHZ.
2. Simulate the quartz crystal microbalance system by develop a suitable modeling software.
3. Control physical properties of crystal by Butterworth Van dyke (BVD) equivalent circuit using suitable software and get impedance characteristics for different quartz crystal frequencies overtones.

1.5 Research Significance

The advantages that the QCM provides for development of the above domain areas is a sensitive detection capability for surface mass binding and a surface viscoelastic characterization capability for the bound mass, other distinct advantages of the QCM technique are the following:

1. The mass sensing technique eliminates the need for any specific labeling step to be part of the signal transduction mechanism.
2. Signal transduction via the piezoelectric mechanism operates well in complex, often optically opaque solution media.
3. The technique is capable of detecting subtle changes in the solution-surface interface that can be due to density-viscosity changes in the solution, viscoelastic changes in the bound interfacial material, and changes in the surface free energy, to name a few.
4. The electrochemical quartz crystal microbalance (EQCM) variant allows the investigator to apply a potential on the upper metal electrode, thereby creating an electrochemical cell, enabling electro chemical reactions or measurement of processes involving electron transfer. This provides interesting ways to create or probe surface bound mass as we describe in this review.
5. Finally, the technique is relatively easy to use, and the basic equipment is inexpensive to purchase. Although the QCM will not supplant high throughput array technologies for drug or biomaterials screening, it provides the realistic possibility of low throughput arrays, perhaps useful in secondary screening situations.

In this format, the QCM provides interesting ways to characterize the mass and visco-elastic properties of complex thin biopolymer films incorporating bimolecular systems at surfaces in the solution of choice, both during their formation and once formed and under perturbations in their environment.

Thus, the QCM technique becomes a useful adjunct to the development of future non-QCM array technologies. It has found use already as a gas phase chemical sensor and metal deposition sensor in vacuum applications and is being developed as a biosensor platform.

For these reasons, the technique is currently exhibiting rapid growth outside of its traditional development domain area of analytical chemistry and electro analytical chemistry.

A number of review articles have appeared in recent years that discuss the applications and technical issues involved in QCM use. They range from the perspective of QCM as a fundamental tool in analytical electrochemistry to comparative reviews focused on the newer application areas of biosensors and drug discovery.

In this review the concentrate is on the application of the QCM technique to the study of the formation and characterization of thin but complex biopolymer meric films and biomimetic systems involving biomacromolecules and briefly outline its applications to the study of fundamental biological processes, biosensors for analyte detection, and more complex biomolecular systems, including living cells [3], this study having the following applications listed in Table 1.1.

Table 1.1: QCM Applications [9]

Military & Aerospace Communications Navigation IFF Radar Sensors Guidance systems Fuzzes Electronic warfare Sonobouys	Research & Metrology Atomic clocks Instruments Astronomy & geodesy Space tracking Celestial navigation	Industrial Communications Telecommunications Mobile/cellular/portable radio, telephone & pager Aviation Marine Navigation Instrumentation Computers Digital systems CRT displays Disk drives Modems Tagging/identification Utilities Sensors
Automotive Engine control, stereo, clock Trip computer, GPS	Consumer Watches & clocks Cellular & cordless phones, pagers Radio & hi-fi equipment Color TV Cable TV systems Home computers VCR & video camera CB & amateur radio Toys & games Pacemakers Other medical device	

1.6 Summary

Quartz crystals (SiO_2) are an indispensable component of modern electronic technology. They are used to generate frequencies to control and manage virtually all communication systems. It is the product of the phenomenon of piezo-electricity discovered by the Curie brothers in France in 1880.

Quartz crystal microbalance (QCM) sensors have become a valuable tool for the study of material properties with respect to fluids or solid films. The spectrum of applications related to the use of QCM sensors is continuously broadening, as it is evident from the ever increasing body of published articles in interdisciplinary scientific areas such as thin film materials, electrochemistry, and biosensors. Many scopes should be bound in order to make this project achieve the objectives including Derive the equations of liquid cell for single sided AT cut quartz crystal.

Crystal oscillation ranged between 5 to 30 MHz , Simulate the liquid cell for single sided AT cut quartz crystal with Butterworth Van dyke (BVD) modeling software, a lower sensitivity limit for QCM device will be examined , and Calibrate physical properties of crystal by using suitable software to get impedance characteristics for different quartz crystal thickness and frequencies overtones. In this project we expect that Mass sensitivity increases with increasing frequency (f) of crystal oscillation , Higher frequency (f) crystals that are significantly more mass sensitive increases the effect surface area of the device, utilizing the piezoelectric mechanism in novel ways, and creating higher throughput multiwall devices for commercial applications , and an increase in motional resistance decreases the frequency(f).

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In the last decade, a new analytical method for the in situ investigation of interfacial processes, including electrode processes, has emerged. This method, commonly referred to as the quartz crystal microbalance (QCM), has had a significant impact in numerous research programs. This includes electrochemists, for which the method is referred to as the electrochemical quartz crystal microbalance (EQCM).

These methods rely on the piezoelectric properties of quartz, in particular a single crystal of quartz that has been cut into a thin wafer at an angle of approximately 35 degrees with respect to the polar z-axis of quartz. The word piezoelectric derives from the word piezein, meaning to press. Hence, the piezoelectric effect hinges on "pressure electricity," a phenomenon first observed by Jacques and Pierre Curie when they discovered that mechanical stress applied to the surfaces of certain crystals, including quartz, resulted in an electrical potential across the crystal.

Shortly afterward, the converse piezoelectric effect – a mechanical strain produced by application of an electric potential across the crystal – was discovered. This effect is sometimes referred to as the converse piezoelectric effect. The motor generator properties have long been associated with underwater sound transducers (sonar), and electromechanical devices such as speakers, microphones, and phonograph pickups.

The quartz crystal microbalance earns its name from its ability to measure the mass of thin films that have adhered to its surface. The quartz crystal microbalance generally comprises a thin AT-cut quartz wafer with a diameter of (0.25 - 1.0) inches, sandwiched between two metal electrodes which are used to establish an electric field across the crystal. If an alternating electric field and appropriate electronics are used, the crystal can be made to oscillate at its resonant frequency. Most crystals of current interest resonate between (5 to 30 MHz).

The measured frequency is dependent upon the combined thickness of the quartz wafer, metal electrodes, and material deposited on the quartz crystal microbalance surface. Because the resonance is very sharp, high precision frequency measurements allow the detection of minute amounts of deposited material, as small as 100 picograms on a square centimeter. Mass changes occurring at the QCM surface result in frequency changes according to the well-established Sauerbrey equation, named after the pioneer of this technique for measurement of film thickness.

The signal transduction mechanism of the QCM technique relies upon the piezoelectric effect in quartz crystals, first discovered in 1880 by the Curie brothers, via a pressure effect on quartz. A change in inertia of a vibrating crystal was then shown by Lord Rayleigh to alter its resonant frequency, f . Important subsequent developments were good crystal stability through the use of electric resonators and room-temperature stable AT-cut crystals. In 1959, the QCM was first used in a sensing mode when Sauerbray reported a linear relationship between the f decrease of an oscillating quartz crystal and the bound elastic mass of deposited metal.

Early chemical applications of QCM were to measuring mass binding from gas-phase species to the quartz surface. These represented some of the earliest chemical sensors for moisture and volatile organic compounds, and gas-phase chromatography detectors. In the 1980s, solution based QCM developed as new oscillator technology advanced to measure changes in frequency that could be related to changes in viscosity and density in highly damping liquid media.

The recent success of the QCM technique is due to its ability to sensitively measure mass changes associated with liquid-solid interfacial phenomena, as well as to characterize energy dissipative or viscoelastic behavior of the mass deposited upon the metal electrode surface of the quartz crystal. Anything that has mass can generate a response from a QCM sensor.

The universal response of the device is the reason for the wide range of application of the technology. However, the downside of such universal sensitivity is that you always have a great danger of interferences. For analytical purposes, it is imperative to find ways of getting the QCM sensor to respond only to what you are interested in (i.e. build sensitivity into the device). This usually involves the addition of a sensitive layer on the surface of the crystal [4]. Organic polymers comprise the most common type of coating used with QCM sensors due to their capability to reversibly sorb vapors and liquids [5].

The relative importance of the mass-loading and viscoelastic contributions of the film to the observed QCM response is a subject that has yet to be resolved. In no area have the QCM applications seen such dramatic increase in recent years as in the field of biochemical analysis. QCM devices are routinely used as biochemical and immunological probes [6], as well as for the investigation and/or monitoring of biochemically significant processes. Sensitive, selective detection of biochemically active compounds can be achieved by employing antigen antibody [7], enzyme substrates and other receptor –protein pairs. The potential analytical use of these materials has been reviewed, particularly with respect to the development of biochemical sensors [8].

QCM studies have provided detailed information about the functionalized surfaces developed for a range of biochip and biosensor applications. As example of QCM sensors was fabricated on a single disc of 1-inch (5 MHz) AT-cut quartz crystal sub-strate. The number of QCM sensors on a quartz sub-strate was designed as 4 and the patterns of electrode pair were laid out symmetrically within 1-inch circle as illustrated in Figure 2.1 [9], and the biological sensing method shows in Figure 2.2.

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